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GASIFICATION OF CHARS PRODUCED UNDER SIMULATED in situ PROCESSING CONDITIONS

Quarterly Report for the Period
October–December 1975

by

J. Fischer, R. Lo,
J. Young, and A. Jonke

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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GASIFICATION OF CHARS PRODUCED UNDER SIMULATED *IN SITU* PROCESSING CONDITIONS

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ABSTRACT

This effort, which is part of the Argonne National Laboratory energy program for ERDA, is being directed toward support studies for the national endeavor on *in situ* coal gasification. This task involves the investigation of reaction-controlling variables and product distributions for the gasification of both coals and chars utilizing steam and oxygen. Included in this task is the investigation of the effects of using brackish water as the water supply. The high-pressure char gasification system has been received from the manufacturer and is currently undergoing testing. The types of experiments that would be most useful in their studies have been discussed with two of the three laboratories carrying out field tests of *in-situ* gasification.

SUMMARY

This task has the objectives of providing engineering data and analyses for the char gasification by steam and oxygen under simulated *in situ* processing conditions. The coal samples will be representative of coal at sites being considered for *in situ* gasification field tests. Chars for gasification will be made by pyrolyzing the coals at the low heating rates characteristic of *in situ* gasification processes. The results will be interpreted in terms of field design and resource recovery; thus this work will support the major field projects in the ERDA *in situ* coal program.

A laboratory-scale unit to study the reaction of steam and oxygen with coal and char was completed, installed, and tested in December 1975. This system will be operated at 850°C and 450 psig pressure. At a future date, after replacement of the reactor vessel, its upper operating limit will be 1000°C and 2000 psig. The gasification unit and analytical system are currently undergoing shakedown tests. Experimental work is scheduled to begin in January 1976.

A number of studies will be carried out pertaining to gasification of coals and chars. We will determine the variation of the product distribution as a function of (1) coal devolatilization conditions, (2) reaction temperature, and (3) total pressure. Several of the individual gasification reactions will be studied. These reactions are:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

$$H_2O + C \rightleftarrows CO + H$$

$$CO_2 + C \rightleftarrows 2CO$$

INTRODUCTION

The objective of this project is to determine the reaction-controlling variables and reaction kinetics for the gasification of coals and chars resulting from the pyrolysis of coal in underground gasification. This work is relevant to all underground gasification projects being funded by ERDA. The data obtained from this work will be used in modeling *in situ* gasification systems, in order to understand and interpret field experimental data, and will be used in the design of future field experiments.

In the gasification of coal and char in a laboratory-scale gasifier using steam and oxygen, a number of variables will be investigated that are representative of actual *in situ* gasification conditions. These variables include total pressure, reaction temperature, coal devolatilization conditions, and partial pressure of steam. Quantitative information about gaseous products such as hydrogen, methane, higher hydrocarbons, carbon monoxide, and carbon dioxide will be measured in order to establish the Btu value of gas obtained by gasification of the coal or char.

The water supply for *in situ* gasification projects will frequently be brackish, containing dissolved or suspended minerals such as carbonates, bicarbonates, halides, and hydroxides of alkali and alkaline earth metals. The catalytic effects of these materials on char gasification will be investigated under conditions likely to be encountered in underground gasification.

In this report, the laboratory-scale reactor system is described. Also, planned studies of the reaction kinetics and the possible effects of brackish water components on the reaction rates are described in detail.

LABORATORY-SCALE CHAR-GASIFICATION SYSTEM

The laboratory-scale reactor system was received from the constructor in late November 1975. It is now undergoing testing and minor modification by the constructor and is expected to be operational in early January, 1976. A schematic diagram of the system is shown in Fig. 1.

The water for steam generation is supplied by a high-pressure (2000 psig) positive-displacement metering pump. This pump provides a variable feed rate (which can be set to a minimum of 5 cm^3/hr). The water flows into a coiled-tube high-pressure steam generator which is encased in a split-type furnace. The steam is then blended with an additional reactant or carrier gas (N_2, CO, CO_2, H_2) prior to entering the reactor. The gas flow is monitored by means of a differential pressure unit, the output of which is connected to a mass flow controller, located on the remote-control console. This mass flow controller drives a pneumatically actuated high-pressure needle valve, which controls the flow of gas. Both the steam and the reaction gas flows can be remotely switched to bypass the reactor, either for flow calibration purposes or for standby conditions.

The reactor vessel (1.6 cm ID x 91 cm long) is constructed of type 316 stainless steel and is rated for a pressure of 450 psig at 850°C.* The reactor is heated using a three-zone split-type tube furnace with 15.25, 30.5, and 15.25 cm long heater sections. Reactor temperatures are monitored by means of a cluster of three thermocouples situated at the center axis of the reactor.

The product stream is cooled in a high-pressure, water-cooled condenser, with the steam and hydrocarbon condensate being collected in a high-pressure separator. The product gas is then dried, let down to atmospheric pressure through a remotely controlled back-pressure regulator, and passed to the analytical section. At this point, the gas is fed to an on-line gas chromatograph and then to a wet-test meter for measurement of total product gas flow. The chromatograph analyzes for H_2, CO, CO_2, and CH_4 in the gas stream. In the future, a sulfur analyzer will be added in order to analyze for H_2S in the product gas.

COORDINATION OF ANL EXPERIMENTS WITH FIELD TESTS

In order to coordinate our experimental efforts with those of laboratories conducting underground field tests, Lawrence Livermore Laboratories (LLL) and

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* At a future date, after replacement of the reactor vessel, its upper operating limit will be 1000°C and 2000 psig.

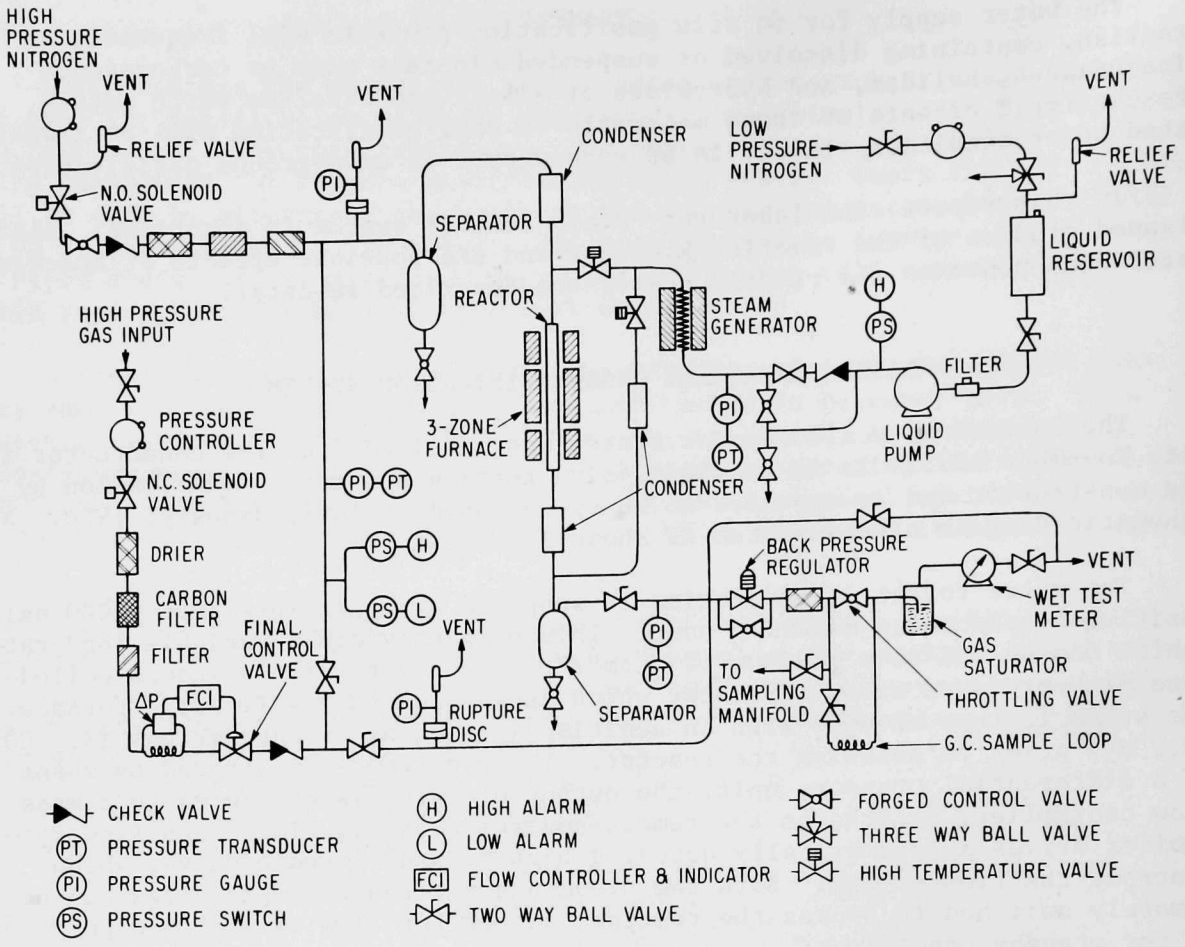

Fig. 1. Schematic Flow Diagram of Laboratory-Scale Char Gasification System

Laramie Energy Research Center were visited.* Following these discussions, an experimental plan (discussed below) has been drawn up to further define the studies to be carried out during approximately the next nine months.

EXPERIMENTAL STUDIES

Three materials will be studied, each being characteristic of the coal being utilized in one of the ERDA-supported field tests. These coals are Pittsburgh Seam, Hanna No. 1 Seam, and a Wyodak-Anderson Seam. The last-mentioned coal has been studied in laboratory tests conducted at LLL. It is similar to the Felix No. 2 coal which will be used in the field tests carried out by LLL. As more core samples of the Felix No. 2 coal become available, this material will be studied in our reactor system, but for the present, the Wyodak coal will be used. The Hanna and Wyodak coals are subbituminous; the Pittsburgh Seam coal is a high-volatile bituminous coal. The last-mentioned coal is also a strongly caking coal and hence will present problems during the devolatilization stage of our studies. This problem will be discussed further in later sections.

* In January, a similar trip will be made to Morgantown Energy Research Center.

The reactor system will be operated at differential conversion rates, *i.e.*, conversion of less than 1% of the input reactant. This has several advantages over an integral reactor. Temperature control is much easier with a differential reactor. At a high conversion rate, a strongly exothermic or endothermic reaction would produce a temperature profile in the reaction bed, making definition of the reaction temperature extremely difficult. At differential conversion rates, temperature uniformity throughout the bed is ensured.

Use of the differential reactor permits reaction rates to be calculated directly from experimental conversion data. The concentrations of reactants and products are essentially uniform throughout the reaction bed; hence, the reaction order can easily be determined by studying the variation of product distribution as a function of initial reactant gas partial pressures. The kinetic information to be obtained for each of the reactions studied includes rate constants, reaction orders with respect to each of the reactants and products, and apparent activation energies.

The chars will be prepared in the reactor in order to prevent exposure to oxygen between the devolatilization reaction and the gasification reaction. A standard set of pyrolysis conditions will be used for the initial experiments of these studies. These conditions will consist of a heating rate of 3°C/min up to the gasification reaction temperature, with pyrolysis carried out in a flow of approximately five liters per hour nitrogen, at atmospheric pressure.

For two subbituminous coals to be studied, the initial particle size of the coal should have little effect on the nature of the resulting char. These coals fragment and form fissures as they pyrolyze. The size of the final char particles is apparently independent of the size of the initial coal particle; this fact must be confirmed, and experiments will be carried out utilizing two differing coal particle sizes, *e.g.*, 1 mm diameter and 5-10 mm diameter. If this variation in starting particle size has little effect on the kinetics of the gasification reactions, the use of an arbitrary standard particle size will be justified.

In the case of the Pittsburgh Seam coal, the starting material swells and forms a coke during pyrolysis. For this coal, a series of particle sizes will be studied in order to find the necessary conditions that will minimize the effects of bulk diffusion limitations upon the gasification kinetics.

It is expected that differing pyrolysis conditions will have an effect on the kinetics of the subsequent gasification reactions. These conditions include rate of heating, the nature of the atmosphere present during pyrolysis, and the total pressure during pyrolysis. Under expected *in situ* gasification conditions, the coal is heated to the final reaction temperature at a rate of approximately 3°C/min. However, experiments will be carried out with heating rates of 1°C/min and 10°C/min in order to determine the effect of pyrolysis rate on the gasification kinetics.

Studies carried out at Lawrence Livermore Laboratory[1] indicate that varying the composition of gas present during pyrolysis of subbituminous coal results in a change in the amount of volatile matter pyrolyzed from

the coal. It is unknown yet whether this effect also extends to the reactivity of the resulting char. Since the pyrolysis gas is expected to contain H_2, CO, and CO_2 as well as nitrogen under *in situ* conditions, experiments will be carried out utilizing each of these components as the atmosphere present during preparation of the chars. These experiments will be carried out at pressures of 1, 15, and 30 atm of hydrogen, carbon dioxide and carbon monoxide, using the Wyodak coal as starting material. If an effect is observed on the kinetics of the steam-char reaction, these experiments will also be made with the Hanna and Pittsburgh Seam coals.

As is true for pyrolysis gas composition, the effects on char reactivity of variations in overall pressure during pyrolysis is unknown. Pyrolysis will be carried out at pressures of 1, 15, and 30 atm of nitrogen and carbon monoxide, using the Wyodak coal as starting material. If an effect is observed on the kinetics of the steam-char reaction, these experiments will also be made with the Hanna and Pittsburgh Seam coals.

The primary reactions to be studied are the char-steam reaction, char-CO_2 reaction, and the water gas shift reaction. The temperature range for the char-steam and char-CO_2 kinetics study will be 400-900°C. Three overall steam pressures will be used--1, 5, and 15 atm. The effect on the kinetics caused by varying each of the char preparation conditions mentioned above will be determined.

The water-gas shift reaction may be strongly catalyzed by chars and by ashes from the chars of the coals expected to be used in field tests. Ingles observed that in the case of chars and ashes prepared from a number of Australian brown coals, the reaction approaches thermodynamic equilibrium at very short contact times.[2] Sintering of this coal ash substantially reduced its activity. He believes that the reaction was catalyzed by the mineral matter present in the coal char, since the rates for this reaction were very low when the reaction was carried out over a relatively pure char prepared from sugar.[3]

The water-gas shift reaction will be studied over chars or coke prepared from each of the three coals proposed for field tests. The devolatilization conditions for these coals will be standardized, most closely simulating those expected in actual underground gasification. Except possibly at very high temperatures, variation in the devolatilization conditions would not be expected to have a great effect on the properties of the mineral matter in these materials. Therefore, no full study of the range of devolatilization conditions is planned. The shift reaction will be studied in the temperature range of 400-900°C, at total pressures of one to fifteen atmospheres.

Ingles[2] also observed that with some ashes prepared from Australian brown coals, the disproportionation reaction:

$$2CO \rightarrow CO_2 + C$$

is catalyzed at temperatures in the range, 600-1000°C. This reaction will be studied in the temperature and pressure range of interest (400-900°C, 1-15 atm pressure) for each of the three carbons of interest in these experiments. As in the case of the water-gas shift reaction, a standard set of devolatilization conditions will be chosen; the full range of variables will not be studied.

The ground water at the Western field gasification sites* is brackish. Analyses of these waters are shown in Table 1. The high levels of sodium, potassium, and calcium indicate that use of these waters as a water source for steam generation might result in an advantageous catalytic effect on the gasification kinetics. On the other hand, the chloride levels might inhibit the primary gasification reactions.

Table 1. Chemical Quality of Groundwater[a] at Western *In Situ* Gasification Sites

	Hoe Creek Site, Wyoming[4]			Hanna, Wyoming[5]
	Overburden	Felix No. 2 Seam	Underburden	Hanna No. 2 Seam
Na	80	75	60	600
K	30	25	60	7
Ca+Mg	1075	96	80	22
Fe	0.51	0.47	0.12	--
$HCO_3^- + CO_3^=$	280	480	448	1100
$SO_4^=$	1100	174	162	400
Cl^-	12.5	12.5	18	40
pH	7.5	7.8	9.3	8.5
TDS[b]	2738	976	1236	1750

[a] Concentrations in mg/liter.

[b] Total dissolved solids.

Simulated groundwaters will be prepared incorporating appropriate levels of Na, K, Ca, HCO_3^-, $SO_4^=$, and Cl^-. Coal will be impregnated with solution for an extended period of time prior to devolatilization. Also, attempts will be made to form an aerosol of simulated groundwater in a hot gas stream just prior to introduction into the reactor. The latter technique would simulate conditions encountered if this brackish water is flash-vaporized on contact with hot char or ash underground. The effects of the presence of these salts on the char-steam and char-CO_2 reactions will be investigated.

* Hanna basin and Hoe Creek site.

REVISED MILESTONES FOR COAL AND CHAR GASIFICATION WORK

1. Gasifier apparatus was received late in November 1975.

2. Installation and functional testing of gasifier in December; preliminary testing of the gasifier and analytical techniques to be completed in January 1976.

3. Preliminary data on kinetic and product distribution from gasification of subbituminous and other coal and char, made at low heating rates, delivered May 1976.

4. Final data on kinetics and product distribution from gasification of coal delivered August, 1976.

5. Data on effects of brackish water constituents on gasification of coal and on the effect of minerals in coal and in surrounding strata on gasification will be delivered December 1976.

6. Semiannual reports will be prepared. In addition, the ERDA contract officer will be provided with informal summary quarterly reports on the status of the work, including data. An annual report will be submitted.

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